COMPARISON OF DRY AND WET OXIDATION PROCESS DURING LOW PRESSURE BORON DIFFUSION WITH BBR_3 IN SOLAR CELL PRODUCTION

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Abstract: This paper deals with replacing a dry oxidation with a wet oxidation process during low pressure diffusion using boron tribromide (BBr_3) in solar cell production. Because the liquid boron trioxide (B_2O_3), a product of a chemical reaction during diffusion, condenses apart from wafers on walls of quartz tube, it is essential to clean the tube after diffusion. This could be done by evaporation of water into the tube after unload or, in order to make the production time shorter, by replacing the dry oxidation with wet oxidation process. In this paper a comparison of the wet and dry oxidation is given with regard to the solar cell production.

Keywords: BBr_3, diffusion, solar cell, oxidation.

1. INTRODUCTION

Production of solar cells from N-type Si has two big advantages compared to production cells from P-type Si. Firstly, N-type material has a higher minority carrier diffusion length because of its higher tolerance to common transition metal impurities. Secondly, the minority carrier life time does not suffer from light induced degradation (LID) due to the boron-oxygen related defects which is frequently found in P-type material. In compliance with this, N-type wafers can be produced more cost effectively than high quality P-type wafers [1,2].

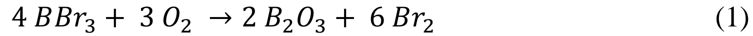
However in spite of these advantages N-type cells are almost never produced industrially due the lack of a cost-effective production process. One of many problems is realization of an emitter on the substrate. The most applicable technology seems to be direct thermal diffusion in open quartz tube furnace using BBr_3 or boron trichloride (BCl_3) because of the price, cleanliness, homogeneity and stability of the process [3 – 5].

The low pressure process of boron diffusion has these advantages over atmospheric pressure diffusion: lower cost owing to smaller consumption of gases and half distance within wafers in the boat, easier achievement of good uniformity of diffusion over the wafer and over the boat, and finally the thickness of a borosilicate glass (BSG) layer is more constant which means that it could be used as a passivation layer.

2. PROCESS OF BORON DIFFUSION USING BBR_3

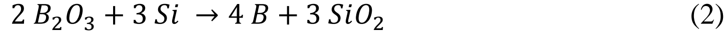
The boron diffusion process using the BBr_3 source for an open-tube furnace can be divided into deposition and drive-in. During deposition the nitrogen is bubbled through liquid BBr_3 at room temperature. Then the doping gas, which is mixture of N_2 and BBr_3, is conducted in to the diffusion tube where a boat with silicon wafers is located. The oxygen (or water vapour) as a reacting gas, and nitrogen as a carrier gas are brought into the tube at the same time. Using the water vapour as the reactive gas instead of oxygen is not very advantageous because water vapour is very reactive and it is hard to achieve good homogeneity of diffusion [3, 5].

In the tube the BBr_3-N_2 blend is mixed with O_2, which causes it to oxidize to form B_2O_3 and bromine (Br):



$$4\,BBr_3 + 3\,O_2 \rightarrow 2\,B_2O_3 + 6\,Br_2 \quad (1)$$

The liquid B_2O_3 condenses not only on the silicon wafer surface but also on walls of quartz tube and on the boat. The chemical reaction gives rise to elemental boron and SiO_2:



$$2\,B_2O_3 + 3\,Si \rightarrow 4\,B + 3\,SiO_2 \quad (2)$$

The SiO_2 reacts with B_2O_3 and a BSG forms on wafers. During a drive-in step a very high concentration of boron occurs at the wafer surface. This results in formation of undesirable Si-B compound (see eq. 3) which is called the boron rich layer (BRL) [3, 5].

$$Si + 6\,B \rightarrow SiB_6 \quad (3)$$

This BRL layer could be converted during oxidation to B_2O_3 and SiO_2 which leads to formation of BSG. The oxidation (wet or dry) could be done before or at the end of drive-in [3, 5].

3. EXPERIMENTAL

For this experiment were used 6'' Czochralski monocrystalline phosphorous-doped N-type silicon wafers after a saw damage removal. The base resistivity was in the range 1 and 3 Ωcm. The samples were placed in the quartz boat on positions represented in the fig. 1 a). The rest of positions were filled up with dummies. The distance within two substrates was 2,15 mm in all cases. Due to the etching process before sheet resistance and a doping profile measurement it was necessary to use 2 wafers positioned next to each other. The number of the sample is the same for both of them because it is possible to expect that they have same properties. A schematic representation of a diffusion process is in the fig. 1 b). Between deposition and drive-in the wet or dry oxidation was done (see tab. 1), in other respects profiles A – C were coincident.

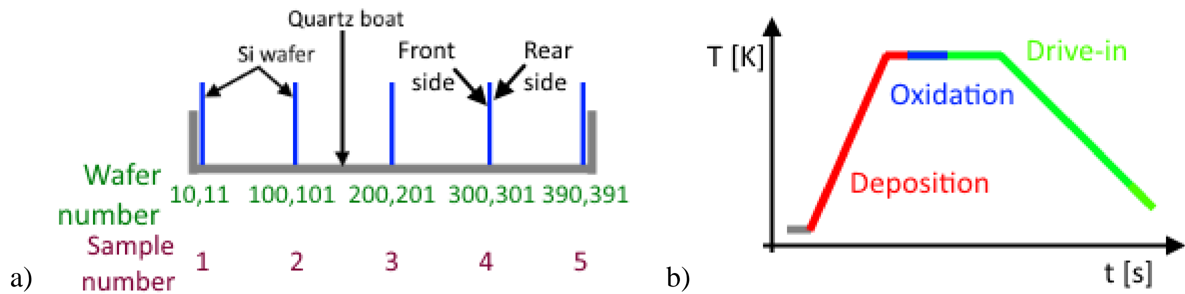


Figure 1: The position of samples in the quartz boat (a) and the profile of the diffusion (b).

Recipe	Type of Oxidation	Steamer	
A	Dry	No	–
B	Wet	Yes	4 min
C	Wet	Yes	6 min

Table 1: The overview of recipes of diffusion profiles.

Removing of the BSG layer was necessary in case of samples used for a sheet resistance (R_{Sheet}) measurement and for a measurement of the doping profile (only for A and C recipe). The BGS layer was etched out in a solution composed of hydrofluoric acid (HF), hydrochloric acid (HCl) and demineralised water. In the case of the rest of wafers the thickness of the BSG layer was measured (only for A and C recipe) and the deposition of passivating layer, using low pressure chemical vapour deposition (LPCVD) of silicon nitride (SiN_x), followed. The implied V_{OC} was measured afterwards before and after annealing.

4. RESULTS AND DISCUSSION

Very significant properties of the emitter of a solar cell are resulting sheet resistance, doping profile parameters, and value of implied V_{OC}. Because BSG layer is used as a passivation layer, the thickness of the layer was measured and its even distribution was investigated.

Because it was not achieved of good homogeneity of the boron layer in case of samples no.5, only results for samples 1 – 4 are always mentioned.

4.1. SHEET RESISTANCE

The resulting sheet resistance was measured by the four point measurement on both sides of the wafer in 5×5 points per wafer side in order to ascertainment the R_{Sheet} average value and its uniformity. In fig. 2 there are shown values of the R_{Sheet} using boxplots in order to compare R_{Sheet} uniformity on the sample. It is evident, that values of the front and the rear side are comparable for the each sample. The average value of R_{Sheet} was ranging from 80 Ω/sq to 99 Ω/sq on front side of wafer, and from 80 Ω/sq to 98 Ω/sq on rear side. The homogeneity of the boron layer was sufficient in case of all recipes (for samples 1 – 4) because the deviation of R_{Sheet} on the one side of the wafer did not exceed 5%.

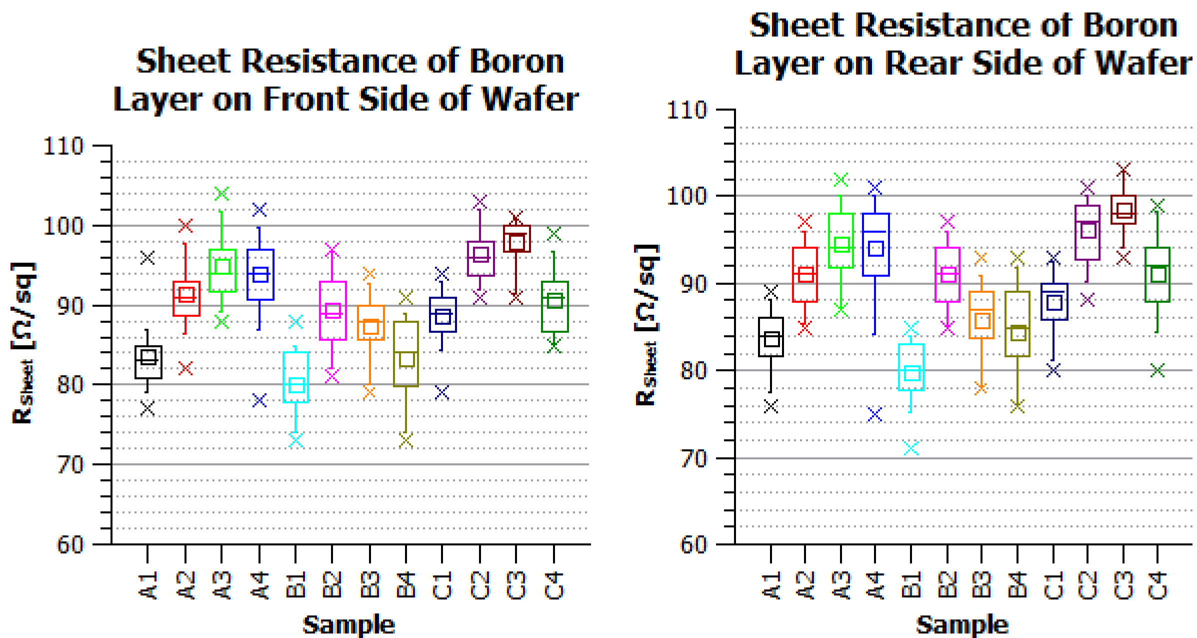


Figure 2: The comparison of emitter R_{Sheet} on the front and on the rear side of the wafer.

4.2. DOPING PROFILE

The doping atom concentration (N_A), the depth, and the shape of doping profile were measured by Electrochemical Capacitance-Voltage (ECV) method. Only samples number 1 and 4 of recipes A and C were determined on account of results from the R_{Sheet} measurement. Doping profiles were determined in the centre of the front side of wafers. The emitter doping profiles are represented in the fig. 3. It is obvious that there was a decrease in the boron concentration near the BSG-Si interface which is caused by different segregation coefficients of B-Si and B-SiO_2. The emitter depth was slightly larger in case of C recipe (0,65 μm) than A-recipe (0,6 μm). The highest boron concentration is around $3{,}2\cdot10^{19}$ cm^{-3} for A recipe and around $2{,}5\cdot10^{19}$ cm^{-3} for recipe B. Also between doping profiles of A and C recipe there is not big difference in the shape of profile.

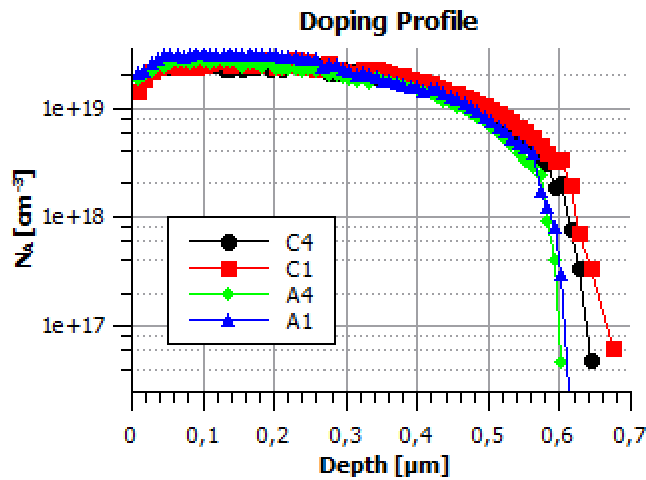


Figure 3: The comparison of doping profiles for recipes A and C.

4.3. THICKNESS OF LAYER OF BOROSILICATE GLASS

The ellipsometry was used for detection of the thickness of the BSG layer (t_{BSG}) for recipes A and C. The thickness was always measured in five points on the front surface of the sample – one point was measured in the middle of the wafer, and remaining 4 points were situated in corners of the wafer, ca. 1 cm from the edge. Ascertained values are shown in the fig. 4 using boxplots in order to compare the BSG layer uniformity. The average value of t_{BSG} was ranging from 44 nm to 68 nm in case of recipe A, and from 67 nm to 83 nm in case of recipe C. Because of much better homogeneity of the BSG layer, the recipe C seems to be a more suitable process. However the thickness of the BSG layer is rather big.

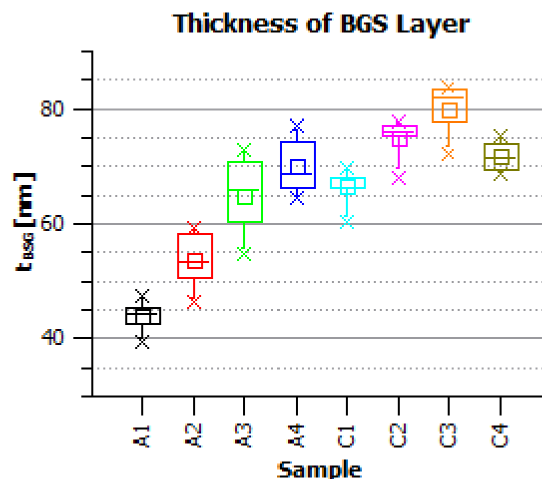


Figure 4: The comparison of the thickness of the borosilicate glass layer.

4.4. IMPLIED V_{OC}

After deposition of the passivation layer of LPCVD SiN_x the implied V_{OC} was measured for all samples before and after annealing using Quasi-Steady-State Photoconductance (QSSPC). The measurements were done on front side of each sample in five points. In the fig. 5 there are shown values of implied V_{OC}. Before annealing the implied V_{OC} was ranging between 0,645 V and 0,651 V for recipe A or from 0,648 V to 0,655 V for recipe B and from 0,654 V to 0,657 V for recipe C. After annealing the implied V_{OC} values increase a little bit. The highest value was reached in case of A recipe (0,689 V) but the best uniformity over boat was reached using recipe B where the average value was ranging between 0,684 V and 0,686 V.

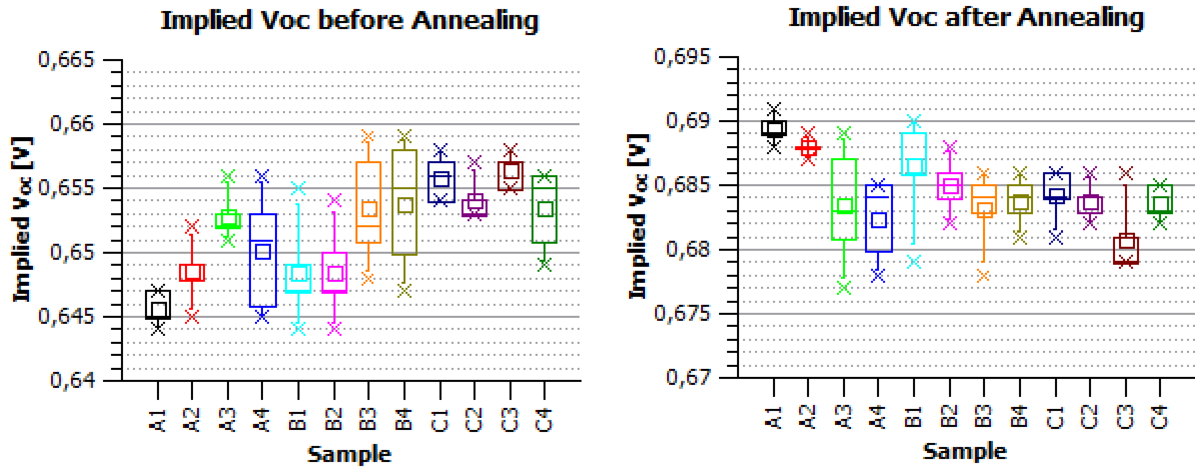


Figure 5: The comparison of implied V_{OC} of the cell before and after annealing.

5. CONCLUSION

The sheet resistance was varying between 80 Ω/sq and 100 Ω/sq independently of the oxidation process. The difference in the shape of doping profile and maximal boron concentration between recipes A and C was minimal. From the measurement of the thickness of BGS layers is evident that after wet oxidation the layer was more uniform. After annealing there was no big difference in implied V_{OC} values among all recipes, values were oscillated around 0,685 V. The dry oxidation process could be replaced with wet oxidation.

ACKNOWLEDGEMENT

The article was supported by project no. FEKT-S-14-2300 A new types of electronic circuits and sensors for specific applications.

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